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Synthèse “one-pot” d’un héli-métallocène ionique de Néodyme.

Application à la catalyse de polymérisation de l’isoprene

One-pot synthesis of an ionic half-sandwich complex of Neodymium. Application to isoprene polymerisation catalysis

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Abstract.

The reaction of one equivalent of $\text{Nd}(\text{BH}_4)_3(\text{THF})_3$ with an half equivalent of dialkylmagnesium in the presence of a stoichiometric amount of pentamethylcyclopentadiene cleanly affords a new kind of half-sandwich of neodymium that is stable toward comproportionation. This strategy can be advantageously applied to generate *in situ* catalysts allowing the controlled polymerisation of isoprene.

La réaction d’un équivalent de $\text{Nd}(\text{BH}_4)_3(\text{THF})_3$ avec un demi équivalent de dialkylmagnesium en présence d’une quantité stoechiométrique de pentaméthylcyclopentadiène conduit de façon

univoque à un hémimétallocène de néodyme d'un nouveau type, stable vis à vis de la comproportionation. Cette stratégie peut être appliquée de façon avantageuse pour générer *in situ* des catalyseurs permettant la polymérisation contrôlée de l'isoprène.

Neodymium / half-sandwich / polymerisation catalysis / *trans*-polyisoprene

Néodyme / héli-lanthanidocène / catalyse de polymérisation / *trans*-polyisoprène

1. Introduction.

Lanthanides-based molecular catalysis has been steadily increasing in the last few years (e.g. see the 2002 special issue of Chemical Reviews, vol. 102, n°6), particularly in the field of polymerisation reactions [1]. Between the classical metallocenes and the more recent post-metallocenes developed for this specific area, the hemi-metallocene - also called “half-sandwich” - framework has attracted much less attention, despite spectacular catalytic abilities [2-4]. The major reason is that the hemi-lanthanidocenes have been until now rather difficult to prepare [5], undergoing comproportionation reactions, especially with the larger elements of the series [2,6], and even in the presence of a bulky cyclopentadienyl ligand [7,8].

Two general strategies have been employed until now to prepare half-sandwich lanthanide complexes: ionic, or σ -bond metathesis [2]. Using the former method, we have shown earlier that half-sandwich lanthanide compounds of formula $(C_5Me_4nPr)Ln(BH_4)_2(THF)_n$ ($Ln = Nd, n = 2$; $Ln = Sm, n = 1$) could be isolated in the borohydride series, taking advantage of the bridging ability of the BH_4 group. However, desolvation and clustering was observed, leading to the formation of hexamers $[(C_5Me_4nPr)Ln(BH_4)_2]_6$ as the crystalline form [9]. On the other hand, the σ -bond metathesis method requires highly sensitive homoleptic LnR_3 precursors ($R = alkyl$ [2], allyl [10], phenyl

[11], or amido group [12]) [13], but it has the advantage to allow the formation of the expected product in one step with a minimal experimental work-up, as the formation of inorganic salts is avoided. However, owing to the basicity of the R group, heating is often necessary to achieve the metathesis reaction, and ligand scrambling may be not completely excluded [5,11]. Very recently, Anwender et al. reported the use of $\text{Ln}(\text{AlMe}_4)_3$ as starting material for half-sandwich complexes via σ -bond metathesis with pentamethylcyclopentadiene $\text{C}_5\text{Me}_5\text{H}$. Most drawbacks of other methods (time of reaction, ligands exchange) are avoided, but the preparation of the precursor as well as the formation of highly reactive AlMe_3 during the reaction both require extreme attention [14]. In contrast, $\text{Ln}(\text{BH}_4)_3(\text{THF})_3$ are stable and easy to handle. They are also recognized as efficient precursors for organolanthanides syntheses [15], and we expected that they could be valuable starting materials for σ -bond metathesis to produce C_5Me_5 -supported compounds.

In this paper we describe the synthesis and characterisation, including X-Ray structure, of a new type of ionic half-sandwich of neodymium, prepared according to a direct *in situ* σ -bond metathesis involving $\text{Nd}(\text{BH}_4)_3(\text{THF})_3$ and $\text{C}_5\text{Me}_5\text{H}$ as starting materials. This ionic complex shows the same efficiency for the controlled polymerisation of isoprene as its neutral homologue, which synthesis requires by contrast the previous preparation of KC_5Me_5 .

2. Results and discussion.

2.1. Synthesis of complex 2

First attempts of a direct reaction between $\text{Nd}(\text{BH}_4)_3(\text{THF})_3$ (**1**), and $\text{C}_5\text{Me}_5\text{H}$ were made, but failed, even after a prolonged reaction time (^1H NMR monitoring). On the other hand, we recently established that Ln-alkyl bonds are readily obtained from the reaction of a $[\text{Ln}]-(\text{BH}_4)$ moiety with an alkylating agent, enabling the preparation of highly efficient catalytic systems for the polymerisation of non polar monomers [3b,15-18]. Following this

idea, a solution of BEM (nBuEtMg) was added to a 1:1 toluene mixture of C₅Me₅H and **1** at room temperature. A clean reaction took place within a few minutes, affording a compound consisting of one C₅Me₅ ligand for 3 BH₄ groups whereas no precipitation of the expected Mg(BH₄)₂ occurred (scheme 1) [19].

Scheme 1

After slow concentration of the toluene solution, light blue single crystals could be isolated. X-ray structure determination allowed to establish [(C₅Me₅)Nd(BH₄)₃]₂[Mg(THF)₆] (**2**) as molecular formula for the isolated complex [20]. It must be emphasized that this unprecedented synthetic method, that we call the “borohydride/alkyl route”, requires very mild experimental conditions, and ordinary lanthanides precursors.

2.3. X Ray structure of [(C₅Me₅)Nd(BH₄)₃]₂[Mg(THF)₆] (**2**)

Complex **2** is a trinuclear ionic compound comprising two anionic half-neodymocene trisborohydride [(C₅Me₅)Nd(BH₄)₃][−] moieties and one cationic hexa-THF magnesium [Mg(THF)₆]²⁺ adduct (Fig. 1) that alternate in the unit cell without direct cation – anion interaction. The asymmetric unit contains two slightly different trimetallic Nd/Mg/Nd entities. The Nd anions have a pseudo tetrahedral tri-legged piano-stool geometry. It is noteworthy that the Nd–B distances (six coordination) fall in a narrow range of 2.582(5) to 2.586(5) Å, typical of monomeric borohydrido complexes bearing a tridentate Nd–(η³-H)₃B-H terminal group [15,21]. Hydrogens belonging to borohydride groups could be located, geometric parameters (B-H, Nd-H distances, and B-H-Nd angles) confirm the η³-mode, likely distorted, however [17,22]. The Mg cation exhibits the octahedral geometry with oxygen atoms of THF molecules.

The absence of coordinated THF to the neodymium atom points out the higher affinity of the lanthanide towards ionic ligands.

Figure 1

Though structurally characterized molecular $\text{Cp}^{\text{R}}\text{LnX}_3^-$ (Cp^{R} is a substituted cyclopentadienyl ligand) species have been observed occasionally [23], the borohydride anionic $[(\text{C}_5\text{Me}_5)\text{Nd}(\text{BH}_4)_3]^-$ is singular. Moreover, we checked (^1H NMR, C_6D_6) that a solution of **2** prepared in our one pot procedure remained unchanged after 20 h at 75 °C (see experimental). Thus, $(\text{C}_5\text{Me}_5)\text{LnX}_3^-$ appears as a stable molecular entity in the borohydride series, with respect to comproportionation or clustering. The ionic trinuclear structure of compound **2** is comparable to that of $[\text{Mg}(\text{THF})_6][\text{Nd}(\text{allyl})_4]_2(2\text{THF})$, obtained by ionic metathesis, with discrete $[\text{Mg}(\text{THF})_6]^{2+}$ cation and allyl neodymate anions [24].

2.4. Isoprene polymerisation

Precatalyst **2** combined with 1 equivalent of BEM afforded a very efficient initiator toward isoprene polymerisation (Table 1), which catalytic behaviour was fully comparable to the one obtained from neutral $(\text{C}_5\text{Me}_5)\text{Nd}(\text{BH}_4)_2(\text{THF})_2$ (**3**) with 1 equivalent of BEM using a procedure that we previously described [3b]. As can be seen from the M_n values, such polymerisation process was found to be living with one growing chain per Nd.

Table 1

The livingness of the latter catalyst is confirmed by a double feed monomer experiment, showing the typical GPC profiles (Fig. 2) [25].

Figure 2

Ultimately, we found that a mixture made of **1**, C₅Me₅H, and BEM in the 1/1/1.5 ratio shows a very similar reactivity towards isoprene. In that latter case, it is likely that i) a half sandwich compound forms in solution (precatalyst **2'**, Table 1) from the reaction between **1**, C₅Me₅H, and 0.5 equivalent of BEM, ii) the subsequent combination of this precatalyst with the residual equivalent of BEM affords the catalytic species (Scheme 2). The somewhat lower activity of this catalytic system is tentatively ascribed to the number of THF molecules initially coordinated to the neodymium atom.

Scheme 2

According to the high and very close levels of *trans*-selectivity, along with the controlled macromolecular data, the three different pathways most probably involve the same half-sandwich catalytic species [26]. One can thus propose that **2** dissociates in solution in the presence of 1 equivalent of BEM (Scheme 3).

Scheme 3

To generalize the above procedure, additional *in situ* experiments were carried out with 1,2,4-Ph₃C₅H₂ and C₅H₅ as ligands (precatalysts **4'** and **5'**, respectively): in both cases, the process was much less controlled and the activity was lower (Table 1), showing the specific role played by the presence of a C₅Me₅ ligand in the coordination sphere of the neodymium atom for such catalysis.

3. Conclusion.

To conclude, we report herein that the “borohydride/alkyl route” is an elegant alternative for the preparation of half-sandwiches of early lanthanides, enabling a one pot and high yield synthesis and starting with simple precursors. By using this method, it is possible to prepare *in situ* and very easily sophisticated lanthanide-based catalysts, but also to simply evaluate the impact of a Cp^R ligand upon a catalytic process in a high throughput screening context.

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[19] Preliminary ^1H NMR experiments: 10.0 mg of **1** (25 μmol) and 1 equiv. of $\text{C}_5\text{Me}_5\text{H}$ (3.4 mg) were weighed in an NMR tube and 0.4 mL of C_6D_6 was added. No reaction took place as shown by the presence of both unreacted starting materials in the ^1H NMR spectrum, even after warming for a prolonged time. 0.5 equivalent of a solution of BEM (7 mg) was added. Immediately, the solution turned pale blue and no precipitation (especially of any uncoloured inorganic salt) was observed. δ (ppm) = 61.5 (br, 12H, BH_4 , $\nu^{1/2} = 800$ Hz), 8.22 (s, 15H), The paramagnetic THF signals could be depicted (2.45 and 1.02 ppm) but the presence of hexanes (BEM solvent) prevented an accurate integration. The spectrum remained unchanged after 20 h at 75 $^\circ\text{C}$.

Bulk synthesis: $[(\text{C}_5\text{Me}_5)\text{Nd}(\text{BH}_4)_3]_2[\text{Mg}(\text{THF})_6]$ (**2**): 291 mg (0.53 mmol) of a solution of BEM diluted in 5 mL of toluene were added dropwise, at room temperature, to a solution of **1** (430.0 mg, 1.06 mmol) and $\text{C}_5\text{Me}_5\text{H}$ (195 mg, 1.43 mmol) in toluene (30 mL). The mixture turned from light purple to blue immediately. After 12 h stirring at room temperature, the resulting blue solution was filtrated to eliminate the insoluble residues present in very small quantities (ca 20 mg). The solution was concentrated of one third and after 12 h, a crop of well-formed crystals (60 mg) could be collected. The mother liquor was then concentrated to ca 2 mL, providing a blue crystalline powder which was rinsed twice with pentane and finally dried under vacuum ($m = 402$ mg). Complex **2** was found quite soluble in aromatic solvents. Total yield: 83.3 %. Anal. Calc. $\text{C}_{44}\text{H}_{102}\text{B}_6\text{O}_6\text{Nd}_2\text{Mg}$: C,

47.80; H, 9.20. Found: C, 46.84; H, 9.88. ^1H NMR (C_6D_6) δ : 63.8 (v br, 12H, BH_4 , $\nu^{1/2}$ = 600 Hz), 8.28 (s, MeCp, 15H), 1.57 (s, THF, 12H), 0.54 (s, THF, 12H).

[20] Compound 2 ($\text{C}_{44}\text{H}_{102}\text{B}_6\text{MgNd}_2\text{O}_6$) crystallizes in the monoclinic space group $\text{P}2_1$ with a = 11.064(2), b = 30.027(4), c = 17.525(3) Å, β = 106.586(2)°, V = 5580(2) Å³, and ρ = 1.315 g cm⁻³ for Z = 4. CCDC-606630 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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[25] Polymerisation procedure: in a typical polymerisation, 5 mg (0.01 mmol) of catalyst precursor 2 was weighed in a glove box, in a 20 mL flask. Dry toluene (1 mL), BEM (5.5 mg, as a 20% solution in hexanes), and freshly distilled isoprene (1 mL, 10 mmol), were added in this order via syringes into the flask. The reaction mixture was magnetically stirred at 50 °C for 2 h. The polymerisation reaction was terminated as follows: the viscous

mixture was diluted in standard toluene (2 mL) and the resulting solution was poured into ethanol. The precipitated white polymer was filtered out, and dried under vacuum for 24 h. In the case of the double feed of monomer, the same procedure was carried out, but the mixture was stirred 24 h at 20 °C. A part of the mixture was then taken away for analysis, and a second crop of isoprene was added in the flask. The polymerisation was allowed to continue 24 h in the same conditions. After that time, the polymeric material was recovered as above.

[26] According to an NMR study, the active species involved in the catalytic process is probably a $[(C_5Me_5)Nd]-(\mu-BH_4)-Mg$ bimetallic one, see ref 3b.

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Captions.

Scheme 1. Synthesis of the half-sandwich complex **2**.

Scheme 2. Synthesis of *trans*-polyisoprene from **2**, **2'** and **3**, in combination with BEM.

Scheme 3. Formation of the active species from anionic half-sandwich moiety of complex **2**.

Fig. 1. ORTEP structure of one of the two entities of the asymmetric unit showing the molecular structure of **2** (thermal ellipsoids at the 30% level; non-BH₄ hydrogen atoms omitted for clarity).

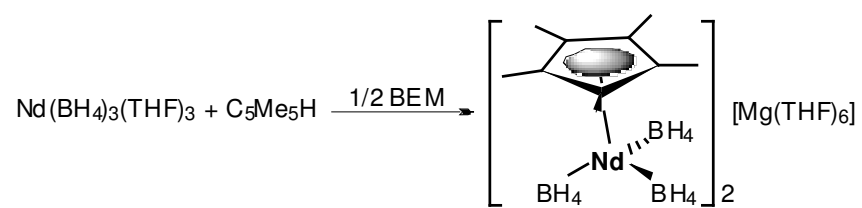
Fig. 2. GPC profiles before (plain line) and after (dot line) the second feed of isoprene obtained with **3**/1 BEM catalytic system.

Table 1. Isoprene polymerisation with (borohydrido half-neodymocene / BEM) catalysts

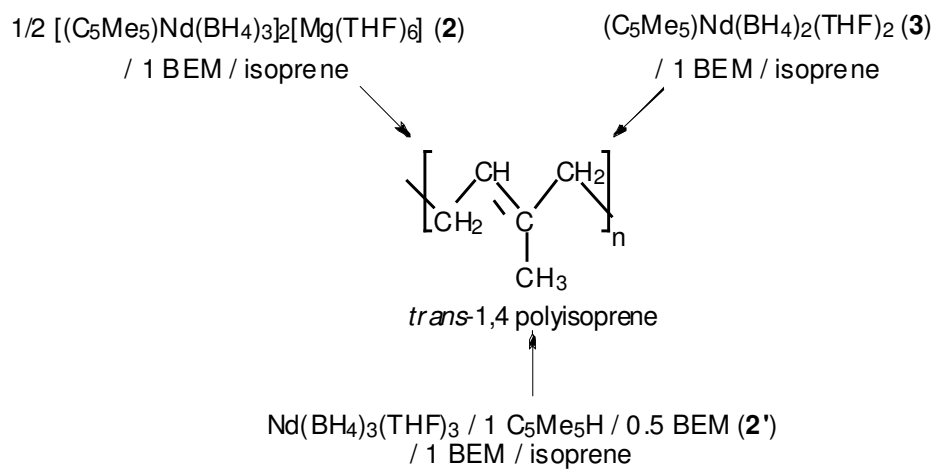
Table 1.

| Catalytic system ^a | Yield [%] | Rate of <i>trans</i> -PI [%] ^c | <i>Mn</i> ^d | <i>Mw/Mn</i> | <i>Mn</i> _(calc.) ^e |
|-------------------------------|-----------------|---|------------------------|--------------|---|
| 2 /1 BEM | 84 | 98.2 | 58200 | 1.16 | 56000 |
| 2' /1 BEM | 68 | 98.0 | 46500 | 1.16 | 48800 |
| 3 /1 BEM | 80 | 97.4 | 52300 | 1.18 | 53700 |
| 4' /1 BEM | 43 | 95.7 | 45300 | 1.48 | 61800 |
| 5' /1 BEM | 60 ^f | 91.4 | 25300 | 1.90 | 40100 |
| 1 /1 BEM ^g | 87 | 95.5 | 58200 | 1.35 | 52100 |

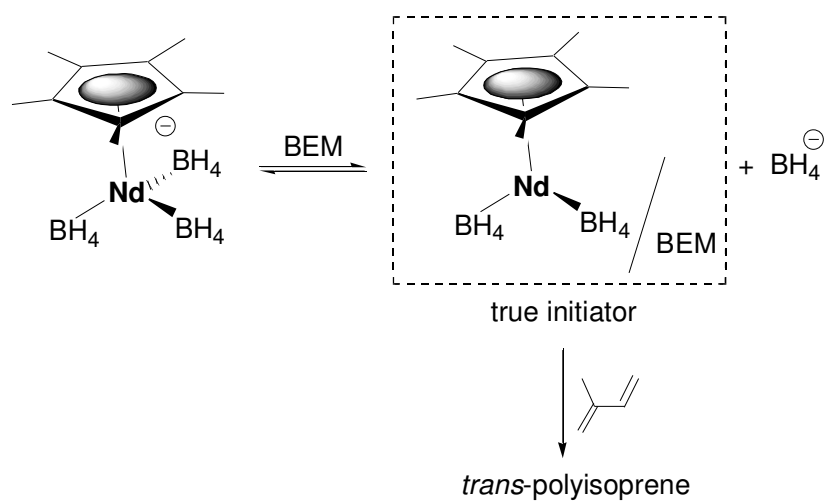
^aConditions: 10 μ mol Nd, 1 mL toluene, [monomer]/[Nd] = 1000, T = 50 °C, t = 2 h. ^b*In situ* prepared precatalyst Nd(BH₄)₃(THF)₃/HCp^R/0.5 BEM, **2'**: Cp^R = C₅Me₅, **4'**: Cp^R = 1,2,4-Ph₃C₅H₂, **5'**: Cp^R = C₅H₅. ^cDetermined by both ¹H and ¹³C NMR integrations (see ESI). ^dDetermined by Steric Exclusion Chromatography calibrated with PS standards. ^e([monomer]/[Nd]) x 68 x (yield %). ^ft = 24 h. ^gsee ref 27.



Scheme 1



Scheme 2



Scheme 3

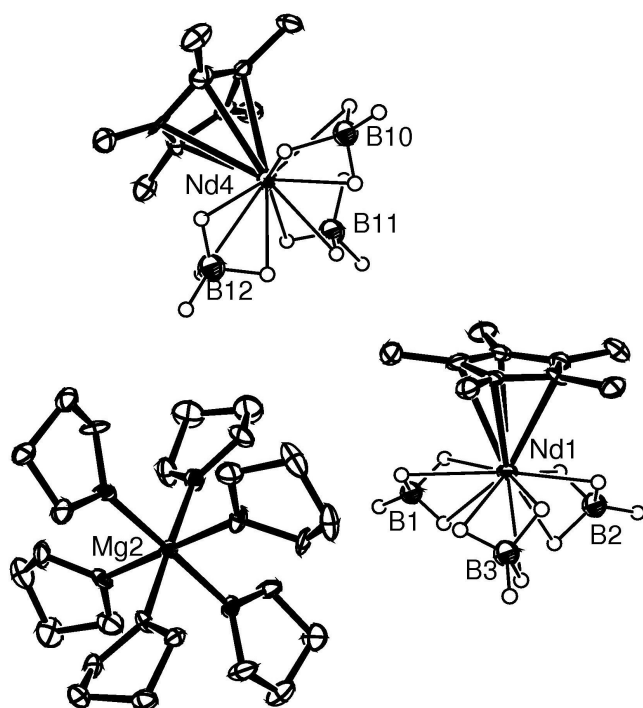


Figure 1

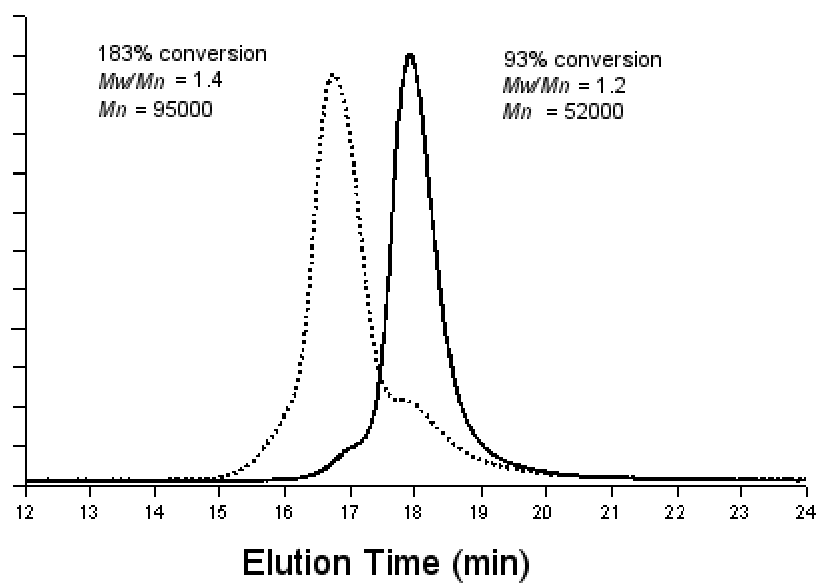


Figure 2